IMR-634

AD 713714

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ON THE INVERSE ISOTOPE EFFECT IN DISSOCIATIVE ATTACHMENT OF
ELECTRONS IN METHANE (U)

by

T. F. O'Malley

June 1967

D D C

1970

**GENERAL
RESEARCH** | CORPORATION

P. O. BOX 3587, SANTA BARBARA, CALIFORNIA 93105

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Sharp and Dowell[1] a little while ago reported observations of dissociative attachment of electrons to methane (CH_4) and deuterated methane (CD_4). They measured the cross section for the formation of H^-, CH_2^-, and the corresponding deuterated species. For the isotopic dependence of the cross section peaks, they found the two relations

$$\sigma_{H^-}(CH_4) \simeq 0.8\sigma_{D^-}(CD_4) \tag{1}$$

while

$$\sigma_{CH_2^-}(CH_4) > 100\sigma_{CD_2^-}(CD_4) \tag{2}$$

The relation (2) is very similar to that found by Schulz and Asundi[2] in H_2 at 3-1/2 eV, and in the same direction as that found earlier in H_2 by Rapp, Sharp, and Briglia[3] at 10 eV which has been well explained theoretically.[4,5] The relation (1), however, which is in the opposite direction to those previously observed and was therefore called an __inverse isotope effect__, was said by the authors not to be understood.

It is the purpose of the present note to point out that the so-called inverse isotope effect exemplified by (1) is the easier of the two to explain, and is simply the $m^{1/4}$ dependence, which is explicitly predicted by the theory[6] whenever the autoionization width Γ_a of the quasistationary final state of the molecule is small (a normal situation for atomic quasistationary states). The expression for the cross section for dissociative attachment from the ground vibrational state is now well known.[6,7] For the present purpose we consider that the cross section is given for a particular system with the normal isotopic components. Now if different isotopes are substituted, we denote by m the ratio of the new reduced mass of the vibrating system to that for the system with normal isotopes. The cross section for attachment from the ground state, given in Ref. 6, when expressed in terms of m and the parameters of the normal system becomes

$$\sigma(m) = C \frac{\Gamma_a}{\Gamma_d} m^{1/4} \exp(m^{1/2}) \left[\frac{- (E - E_o)^2 + \frac{1}{4} \Gamma_a^2}{\frac{1}{4} \Gamma_d^2} - \rho(E) \right] \tag{3}$$

C here stands for a kinematic factor of the order of a few times 10^{-16} cm^2, Γ_a is the width for autoionization, Γ_d (the observable width of the cross section) is a partial dissociation width, and $\rho(E)$ is twice the imaginary part of the final state phase shift. ($e^{-\rho}$, the survival factor, is the probability of dissociating before autoionization takes place.[7])

It is clear at once that the preexponential factor $m^{1/4}$ is capable of explaining the observed "inverse isotope effect" (1). Whenever Γ_a, the autoionization width, is sufficiently small, then in (3) both the Γ_a^2 term and the more important ρ term (which is linear in Γ_a) are negligible,[6] and the value of the exponential at its peak (E = E_o) is equal to 1. It then follows that

$$\sigma_{peak} = C(\Gamma_a/\Gamma_d)m^{1/4}$$

Taking a value of 2 for m, the D^- to H^- reduced mass ratio in the present reaction, we immediately find that $\sigma_H = 0.84$ σ_D, which is in quite close agreement with the observed relation[1].

This $m^{1/4}$ preexponential factor which explains the inverse isotope effect is simply a consequence of the normalization of the initial vibrational wave function. This is perhaps most clearly seen by noting that (under the required condition of small Γ_a and ρ) the area under the σ vs E curve determined by (3) is independent of m (and more generally of Γ_d). In other words, increasing the mass ratio m causes the cross section curve to become narrower and higher while leaving the area constant. (This tendency is clearly borne out by the low energy portion--below 9 eV--of Sharp and Dowell's cross section curve.[1])

The reason this particular isotope effect was not observed in previous isotope studies[2,3] was that it happened that Γ_a and consequently ρ was very large for the states involved, i.e., the two lowest H_2^- states.[4,8] It might be asked which is more typical, the $m^{-1/4}$ dependence which follows from small Γ_a ($\ll 1$ eV) or $\exp(-m^{1/2}\rho)$, the large Γ_a (large ρ) dependence. This is not clear yet. For <u>atomic</u> resonances, small autoionization widths of the order of 10^{-2} eV, or even less, seem to be the rule.[9] On the other hand, the very few cases of diatomic molecular resonances studied[4,10] seem to show ionization widths of tenths of volts and even volts for the most part.[11] For the methane state described by (1), it follows from (3) and the observed cross section magnitude of 10^{-19} cm^2, that Γ_a must be only a few times 10^{-4} eV, a value very much on the small side.

As a word of caution, it should be said that the relation (3) was derived for <u>diatomic</u> systems. It is only to the extent that a polyatomic system such as CH_4 may be described by some kind of normal modes of vibration that the results may be tentatively applied to such a system. For one thing, a lack of knowledge of the normal modes leads to some uncertainty in the reduced mass m (although for the present system this uncertainty does not change the relation (1) very much). Also the presence of any peculiarly polyatomic mechanism might conceivably invalidate the application of the diatomic result (3) altogether.

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6. T. F. O'Malley, Phys. Rev. $\underline{150}$, 14 (1966).

7. J. N. Bardsley, A. Herzenberg and F. Mandl, in Atomic Collision Processes, edited by M.R.C. McDowell (North Holland Publishing Company, Amsterdam, 1964), p. 415.

8. For the third $\overline{H_2}$ resonance at 14 eV (see Ref. 3), the observed mass dependence was presumably due to the vertical onset phenomenon as discussed in Sec. 8 of Ref. 6.

9. See for example R. P. Madden and K. Codling, Phys. Rev. Letters $\underline{10}$, 516 (1963); P. G. Burke and A. Joanna Taylor, Proc. Phys. Soc. $\underline{88}$, 549 (1966).

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11. The extremely narrow states with microsecond autoionization life-times observed recently for complex polyatomic species are something else again and are not fully understood by the present author. See R. N. Compton, L. G. Christophorou, G. S. Hurst and P. W. Reinhardt, J. Chem. Phys. $\underline{45}$, 4634 (1966).